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FLAME-RETARDANT COMPOSITE MATERIALS

Demetrius A. Kourtides
NASA Ames Research Center
Moffett Field, CA 94035

ABSTRACT

This paper describes the properties of eight different graphite composite panels fabricated using four different resin matrices and two types of graphite reinforcement. The resign matrices included: VPSP/BMI, a blend of vinylpolystyrylpyridine and bismaleimide; BMI, a bismaleimide; Phenolic, and PSP, a polystyrylpyridine. The graphite fiber used was AS-4 in the form of either tape or fabric. The properties of these composites were compared with epoxy composites. It was determined that the blend of vinylpolystyrylpyridine and bismaleimide (VPSP/BMI) with the graphite tape was the optimum design giving the lowest heat release rate.

INTRODUCTION

Graphite-reinforce composites have potential applications in advanced aircraft because of their weight saving and performance characteristics. In this study, graphite panels were fabricated using fabric or unidirectional tape. The contribution of the resin matrix to the ultimate performance of these composites was studied, with particular emphasis on thermal and flammability properties. Comparisons were made with state-of-the-art aircraft composite made with epoxy resin. These advanced composites have applications as fire-resistant and light weight panels for ceiling, floors, and sidewalks for aircraft, space station, mass transit vehicles and other transportation vehicles.

DISCUSSION

Resin Chemistry

Four types of resin matrices were evaluated: a) VPSP/BMI (Hercules, Inc.) a bismaleimide/vinylpolystyrylpyridine (VPSP) formulation; b) BMI (Technochemie GMBH), a bismaleimide; c) Phenolic (Cyanamid Co.), and d) PSP (Societe Nationale et Poudres Explosifs), a polystyrylpyridine. Graphite composites made from these resin matrices were compared with a composite made with an epoxy resin as a matrix. The chemistry of these resins is shown in Figures 1 and 2 and is described below.

1. Epoxy Resin: The baseline epoxy resin was an amine-cured polyfunctional glycidyl amine-type epoxy resin.

2. VPSP/BMI: This formulation is based on a formulation of bismaleimide (BMI) and a modified VPSP designated as XU71775.01L (Dow Chemical Co.). This resin has the same oligomer backbone (polystyrylpyridine) as VPSP, but possesses different reactive end groups. The chemistry of the VPSP has been described previously (1, 2, 3). The VPSP/BMI formulation contains seven parts by weight BMI and three parts by weight XU71775.01L. Other reactive materials are added to this formulation to allow hot melt prepreging of the resin. This resin was characterized thermally by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and exothermicity. The DSC of the resin was measured at 10^0 C/min in nitrogen. The endothermic peak at 60-140^0 C is probably due to the evaporation of trace amounts of volatiles. The exothermic cure temperature is at 160-240^0 C with a cure peak at 211^0 C. The resin can be cured at 179^0 C for a longer time. After heating at 179^0 C for 3 hours, the resin showed no residual cure peak. The exothermic peak at 300-360^0 C is probably related to the decomposition of the resin. The TGA of the cured pure resin in nitrogen and air at 10^0 C/min was determined. The resin starts to decompose at about 320^0 C. The char yield at 800^0 C is 52.5%. The TGA of epoxy resin is also shown.

3. BMI: This bismaleimide resin is produced by reacting m-maleimidobenzoic acid chloride with an aromatic diaminocompound in the molar proportion of difunctional amine acid halide 1.4:2. The resulting resin consists of a mixture of a bismaleimide and an aminoterminated monoimide.

4. Phenolic: The chemistry of this phenolic resin is not known.

5. PSP: The reaction scheme for this resin is shown in Figure 2. This resin has been described previously in detail in (4).

Composites Description

The resins just mentioned were used to fabricate eight types of composite panel using two types of reinforcements: a) plain-weave woven graphite fabric (A-193, Hercules, Inc.), and b) unidirectional tape graphite fiber (AS-4, Hercules, Inc.). All panels were fabricated using a honeycomb core (HR-10, Hexcel, Inc.). All composites had a film of polyetheretherketone (PEEK, Imperial Chemical Co.) adhered with a silicone adhesive (Dow Corning X3-5815) on one side. The composition of the panels is given in Figure 1. The thickness of the panels varied slightly depending on the number of plies in each panel. Panels constructed with the graphite fabric had one ply on each side, and panels fabricated with the graphite tape had three plies on each side placed at 0°, 90°, and 0° orientation for maximum strength. The processing of the baseline panel consisting of epoxy-glass fabric with a polyvinylfluoride (PVF) film has been described previously in detail (5). Panels type A, B, E, and F were cocured with the honeycomb core without the use of an additional adhesive. On panels type C, D, G, and H, a polyimide adhesive film (FM-34, Cyanamid Co.) was used to bond the face sheets to the honeycomb. The fabrication procedure and the curing schedule for these composites have been described previously (6). The density of the panels is shown in Figure 2.

TEST RESULTS AND ANALYSIS

A broad range of flammability and thermal tests were conducted to characterize the composites. Three basic flammability properties of the materials were measured: a) propensity to burn, or oxygen index (OI); b) smoke emission, and c) heat release.

Oxygen Index .

The composite panels were tested by the OI in accordance with ASTM D-2863-77(7). The intent of the OI test method is to determine the relative flammability of plastics by measuring the minimum concentration of oxygen in a slowly rising mixture of oxygen and nitrogen that will just support combustion; i.e., OI is defined as the minimum concentration of oxygen and nitrogen that will just support combustion of a material under the conditions of this method.

The test results shown in Figure 3 were as follows: Baseline epoxy-glass fabric/PVF 34.6; panels type A -- VPSP/BMI/Fabric/PEEK 44.3; B -- VPSP/BMI/Tape/PEEK/45.6; C -- BMI/Fabric/PEEK 35.7; D -- BMI/Tape/PEEK 45.0; E -- Phenolic/Fabric/PEEK 38.8; F -- Phenolic/Tape/PEEK/36.9; and G -- PSP/Fabric/PEEK 40.3.

Panel D-BMI/Tape/PEEK had the highest oxygen indes of all the panels tested, followed by Panel A-VPSP/BMI/Fabric/PEEK. The baseline epoxy-glass fabric/PVF had the lowest oxygen index.

Smoke Emission

The smoke emission characteristics of the panels were determined by heating the composites in the NBS Smoke Chamber and the Ohio State University (OSU) heat-release apparatus (8). In this method, the specimen to be tested is injected into an environmental chamber through which a constant flow of air passes. The specimen's exposure is determined by a radiant heat source adjusted to produce the desired total heat flux of 3.5 W/cm~ on the specimen. The specimen is tested so that the exposed surface is vertical. Combustion is initiated by a piloted ignition. The smoke is measured with a photoelectric tube mounted on top of the apparatus. The smoke density is calculated by integrating the light transmission loss over the length of the run.

Specify optical density,

$$\text{maximum}=D_s=\frac{V_2}{AL}\int_0^t \text{Log}_{10} \frac{(100)}{(Plt)} \frac{T_o}{T_i} dt \quad (1)$$

Ds = specific optical density, t = time V2 = volume of air, 2.4 m^3/min A = area of sample, 232.3 cm2 L = length of light path, 0.93 m Plt = percent of light transmission Ti = inlet temperature To = outlet temperature dT = time interval. The test results are given in Figures 4-6. The baseline epoxy-glass fabric/PVF composite had the highest smoke evolution of all composites tested. Panel type H (PSP/Tape/PEEK) had the lowest smoke evolution. The relative ranking of the composites in terms of increased smoke density at 90 sec is as follows: panels type H, B, D, F, C, A, E, G, and Baseline.

Heat Release

The heat-release rates of the composite panels were determined using the OSU Release Calorimeter (8) using a revised test method (9). In this procedure, the specimen to be tested is injected into the environmental chamber through which a constant flow of air passes. The specimen's exposure is determined by using a calibrated calorimeter on a radiant heat source adjusted to produce the desired total heat flux of 3.5 W/cm^2 on the specimen. The temperature difference between the air entering the environmental chamber and that leaving is monitored by a thermopile having three hot, and three cold, 32-gauge Chromel-Alumel junctions. The hot junctions are spaced across the top of the exhaust stack. The cold junctions are located in the pan below the lower air-distribution plate. Heat-release rates are calculated from the reading of the thermopile output voltage at any instant of time as

$$HRR=\frac{(V_m-V_b) \times K_h}{0.02323 \text{ m}^2}$$

HRR = heat-release rate, kW/m^2
Vm = measured thermopile voltage, mV
Vb = "blank" thermopile voltage test obtained by a run conducted with an empty sample holder assembly
Kh = calibration factor, kW/mV

The integral of the heat-release rate is the total-heat release. According to regulations for aircraft (10), the total-heat release over the first 2 min of sample exposure shall not exceed 65 kW-min/m^2 and the peak-heat-release rate shall not exceed 65 kW/m^2. Figures 7 and 8 give the total heat release of the composite panels when exposed at a heat flux of 3.5 W/cm^2. The peak heat-release rate in kW/m^2 of the panels was: baseline epoxy-glass fabric/PVF 82; panel types A -- VPSP/BMI/Fabric/PEEK 57; B -- VPSP/BMI/Tape/PEEK 51; C -- BMI/Fabric/PEEK 84; D -- BMI/Tape/PEEK 91; E -- Phenolic/Fabric/PEEK 80; F -- Phenolic/Tape/PEEK 83; G -- PSP/Fabric/PEEK 99; and H -- PSP/Tape/PEEK 67.

According to these test results, of the nine panels tested, only panel type B (VPSP/BMI/Tape/PEEK) met the above criteria. The total-heat release of this composite was 62 kW-min/m^2 and the peak-heat release rate was 51 kW/m^2. Panels types A and H, with heat release of 66 and 67 kW/m^2, respectively, were marginal failures. The flexural strength, flatwise tensile strength and peel strength of the composites are shown in Figures 11 and 12.

CONCLUSION

To rank the composites, one should consider all of the materials parameters and assign weight to each specific parameter or measurement. Recent studies (9) have indicated that a low rate of heat release or fuel contribution is one of the most important considerations when using composites in critical applications such as aircraft. Based on these observations, the following conclusions may be drawn from this study:

1. The highest total-heat release and heat-release rates were measured with the baseline epoxy composite panel. This panel also exhibited the highest smoke evolution and lowest oxygen index of all the composites tested.

2. The type B panel (VPSP/BMI/Tape/PEEK) exhibited the lowest heat-release rate and total-heat release. It was the only panel tested which meets the performance criteria of maximum heat-release rate of 65 kW/m^2 and maximum total heat release in 2 min of 65 $kW\text{-}min/m^2$. This composite panel measured the highest oxygen index of all the panels.

3. The lowest smoke evolution was measured in panel type G (PSP/Fabric/PEEK) and panel type D (BMI/Tape/PEEK).

4. All the graphite composites exhibited oxygen indices significantly higher than the baseline panel, indicating that the graphite panels will exhibit lower relative flammability. Composite panels A, B, and D showed the highest indices (44.3, 45.6, and 45.0, respectively), compared to 34.6 for the baseline panel.

5. The aforementioned data indicate that composites fabricated with the VPSP/BMI vinylpolystyrylpyridine/bismaleimide resin exhibited the optimum combination of fire-resistant properties and processing characteristics.

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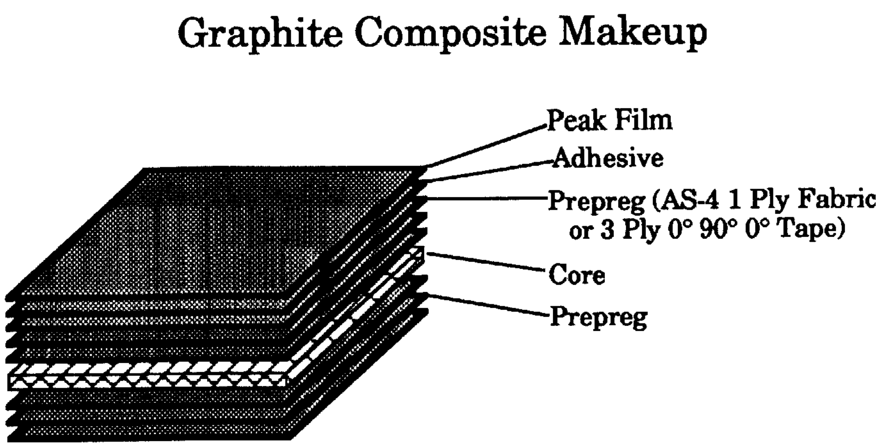

Figure 1

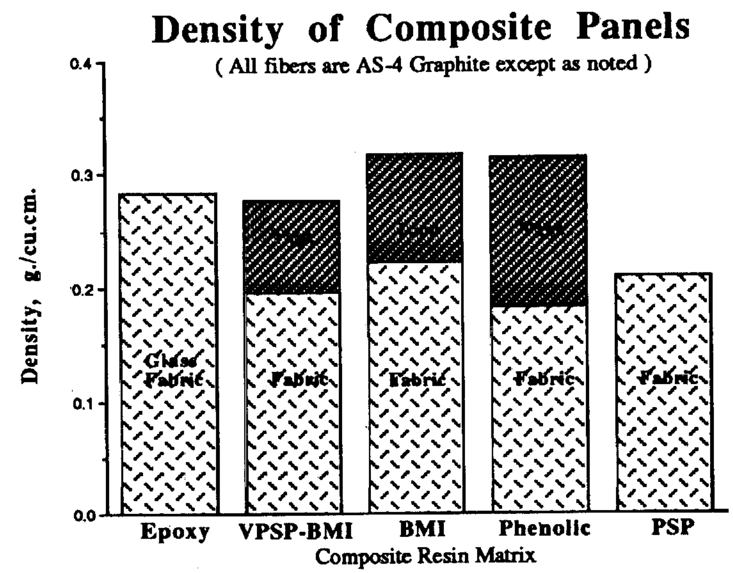

Figure 2

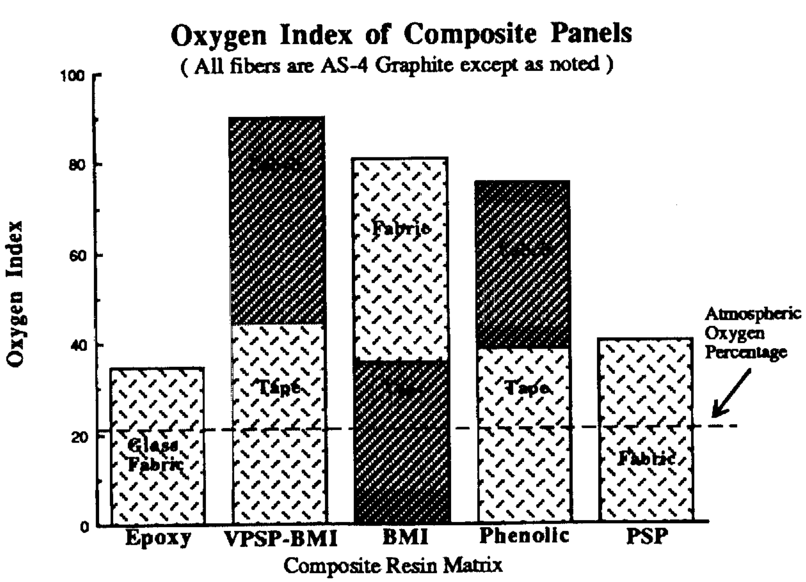

Figure 3

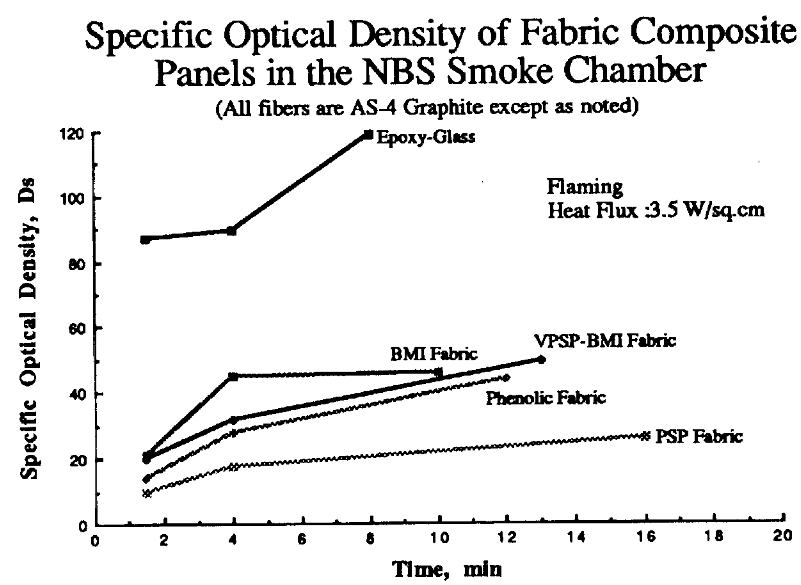

Figure 4

Specific Optical Density of Fabric Composite Panels in the OSU Heat Release Apparatus
(All fibers are AS-4 Graphite except as noted)

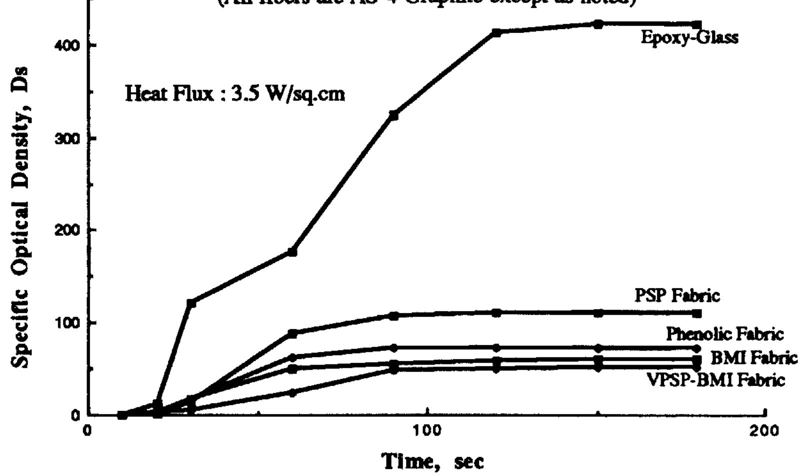

Figure 5

Specific Optical Density of Unidirectional Composite Panels in the OSU Heat Release Apparatus
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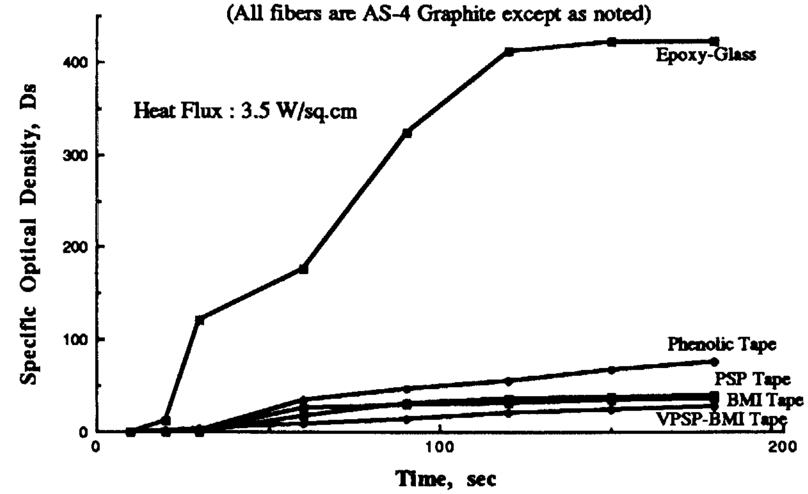

Figure 6

Total Heat Release of Fabric Composite Panels
(All fibers are AS-4 Graphite except as noted)

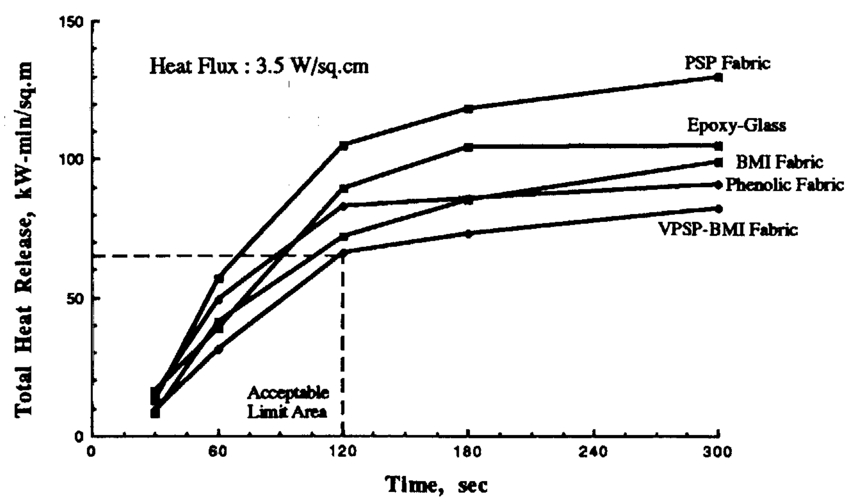

Figure 7

Total Heat Release of Unidirectional Composite Panels
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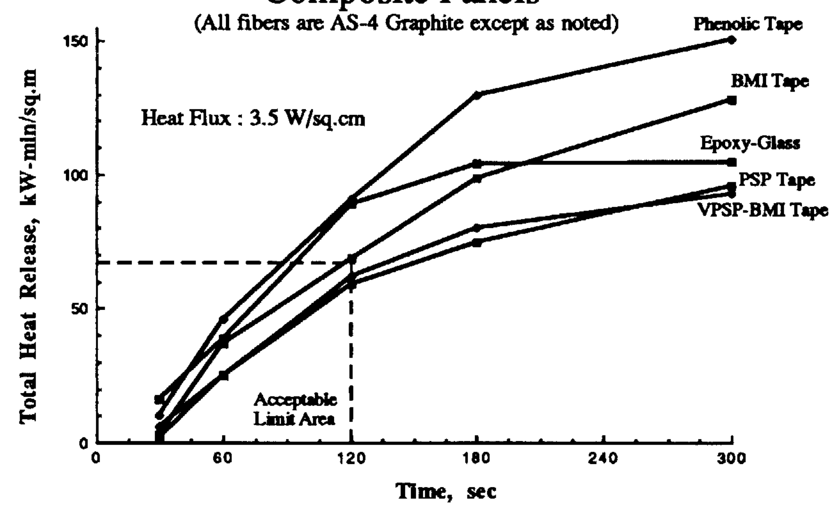

Figure 8

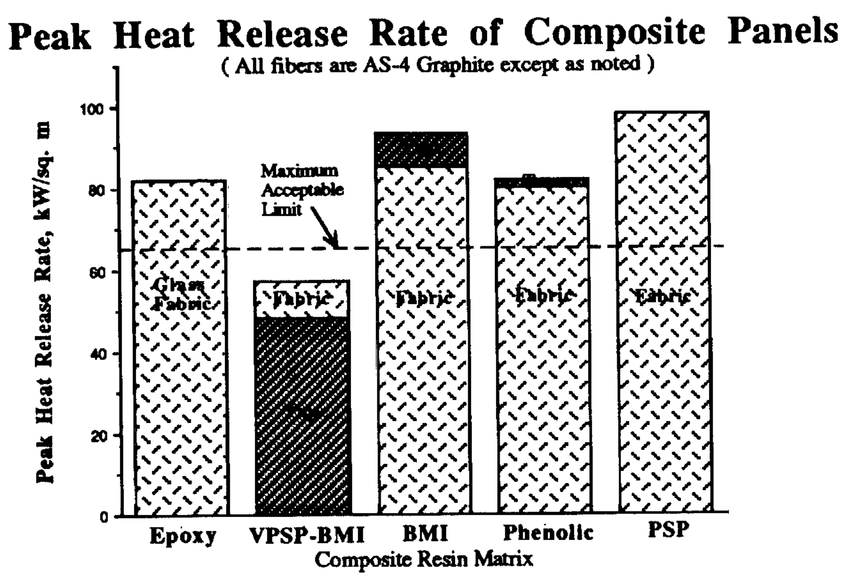

Figure 9

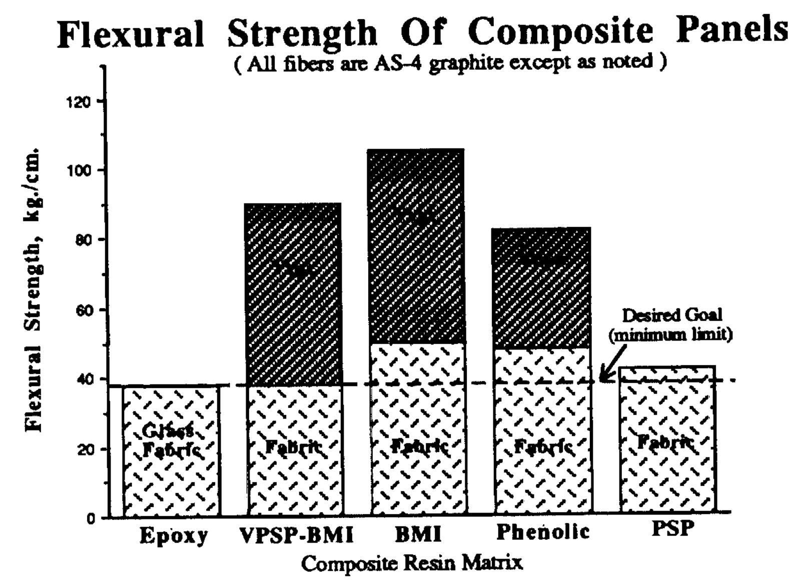

Figure 10

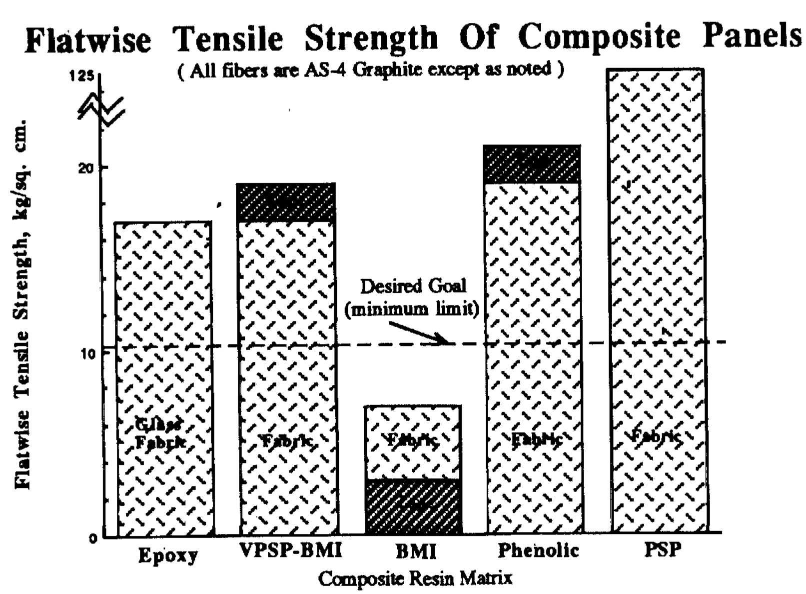

Figure 11

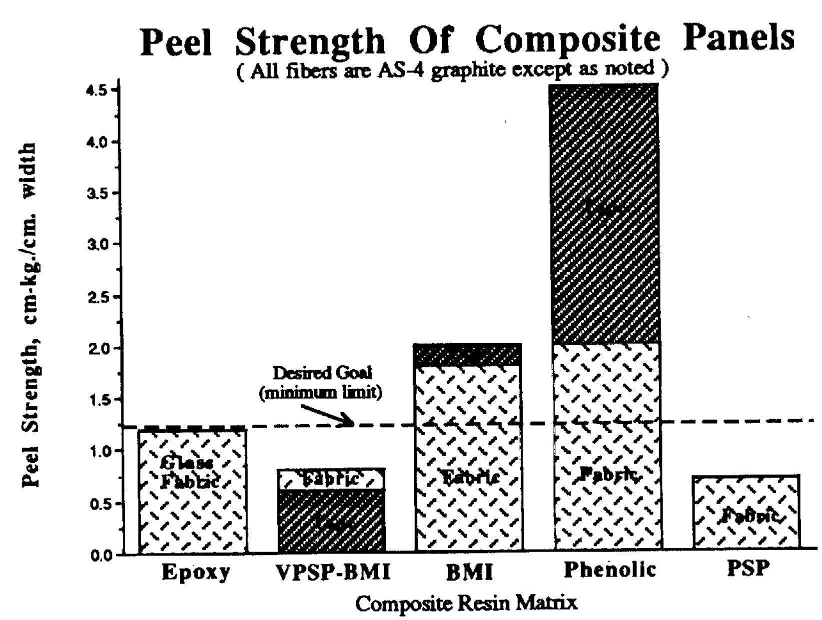

Figure 12